Crystal and Molecular Structure of μ-Pentalene-bis[dicarbonyl(trimethylgermyl)ruthenium]

By **Judith A. K. Howard** and **Peter Woodward,*** Department of Inorganic Chemistry, The University, Bristol BS8 1TS

Reaction of *cis*-[Ru$(GeMe_3)_2(CO)_4$] with cyclo-octatetraene yields a complex [$Ru_2(GeMe_3)_2(CO)_4(C_8H_6)$] which was believed, from spectroscopic evidence, to contain a pentalene species. An *X*-ray diffraction study has shown this to be true, the pentalene being bonded to a nearly linear Ge–Ru–Ru–Ge spine. The two carbon atoms common to both rings are bonded to both ruthenium atoms in the form of a transverse bridge; the remaining two groups of three carbon atoms of the pentalene are each bonded as individual η-allyl interannular units to one ruthenium atom. The trimethylgermyl groups adopt an eclipsed configuration with respect to the bond axis, and the two carbonyl groups attached to each ruthenium atom are likewise eclipsed and are mutually orthogonal. The molecule as a whole has mirror symmetry (not required crystallographically) perpendicular to the Ru–Ru bond. Crystals of [$Ru_2(GeMe_3)_2(CO)_4(C_8H_6)$] are monoclinic, space group $P2_1$, with $a = 9.395(3)$, $b = 22.555(9)$, $c = 10.984(5)$ Å, and $\beta = 96.93(3)°$. The structure was solved by heavy-atom methods from 2 089 intensity data [$I > 2.5\,\sigma(I)$] measured on a four-circle diffractometer and refined to R 0.067.

ALTHOUGH various derivatives of pentalene are known, attempts to synthesize pentalene itself have hitherto proved unsuccessful. Significantly, 1-methylpentalene [1] and 1,3-dimethylpentalene [2] are very unstable and can only be detected spectroscopically at −196 °C. In contrast, the dianion [3] (a 10 π-electron aromatic system) has a well established existence and is known to form transition-metal complexes. The possibility of stabilizing pentalene itself (eight π electrons) as a ligand to a transition-metal cluster has been realised for the first time *via trans*-annular bond formation in cyclo-octatetraene.

Cyclo-octatetraene reacts, in refluxing octane or heptane, with *cis*-[Ru$(GeMe_3)_2(CO)_4$] [4] to give several complexes, one of which (11%) is a pale yellow crystalline solid, m.p. 235 °C (decomp.), formulated as [$Ru_2(GeMe_3)_2(CO)_4(C_8H_6)$]. The various possible structures that may be assigned to this molecule from spectroscopic evidence have been presented in a preliminary communication.[5] We report herein the results of an *X*-ray diffraction study.

EXPERIMENTAL

Crystals of [$Ru_2(GeMe_3)_2(CO)_4(C_8H_6)$] grow as pale yellow plates from hexane. Diffracted intensities were collected from a crystal of dimensions 0.10 × 0.27 × 0.10 mm on a Syntex $P2_1$ four-circle diffractometer according to methods described earlier.[6] Of the total 4 469 independent reflections for $2.9 < 2\theta < 50.0°$, 2 089 satisfied the criterion $I > 2.5\sigma(I)$, and only these were used in the solution and

---

[1] R. Bloch, R. A. Marty, and P. de Mayo, *J. Amer. Chem. Soc.*, 1971, **93**, 3071.

[2] K. Hafner, R. Dönges, E. Goedecke, and R. Kaiser, *Angew. Chem. Internat. Edn.*, 1973, **12**, 337.

[3] T. J. Katz, M. Rosenberger, and R. K. O'Hara, *J. Amer. Chem. Soc.*, 1964, **86**, 249.

[4] S. A. R. Knox and F. G. A. Stone, *J. Chem. Soc. (A)*, 1971, 2874.

[5] A. Brookes, J. A. K. Howard, S. A. R. Knox, F. G. A. Stone, and P. Woodward, *J.C.S. Chem. Comm.*, 1973, 587; also preceding paper.

[6] A. Modinos and P. Woodward, *J.C.S. Dalton*, 1974, 2065.

refinement of the structure. The intensities were corrected for Lorentz, polarization, and X-ray-absorption effects.

RESULTS

Crystal Data.—$C_{18}H_{24}Ge_2O_4Ru_2$, $M = 651.7$, Monoclinic, $a = 9.395(3)$, $b = 22.555(9)$, $c = 10.984(5)$ Å, $\beta = 96.93(3)°$, $D_m = 1.87$, $Z = 4$, $D_c = 1.88$ g cm^{-3}, $U = 2\,310.6$ Å, $F(000) = 1\,264$. Space group $P2_1$. Mo-K_α X-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 40.3 cm^{-1}. The structure was solved for the Ru and Ge locations by vector methods; the remaining atoms were located by successive electron-density difference syntheses. The structure was refined by blocked-matrix least squares, the two crystallographically independent molecules defining each of the two blocks. Hydrogen atoms were incorporated at calculated positions which were not refined. For one methyl group [H(3031-3)] the indications on the electron-density map were too vague to permit location of the atomic centres, so these three atoms were omitted (Table 1). The ruthenium and germanium atoms were ascribed anisotropic thermal parameters, but all the other non-hydrogen atoms were refined isotropically. Atomic-scattering factors were those of ref. 7 for Ru, Ge, C, and O; those for Ru and Ge were corrected for anomalous dispersion[8] (Ru, $\Delta f'$ -1.42, $\Delta f''$ 0.84; Ge, $\Delta f'$ 0.08, $\Delta f''$ 1.80). Scattering factors for hydrogen were from ref. 9. Weights were applied according to the scheme $1/w = \sigma(F_o) + \alpha|F|$, where $\alpha = 0.017$ and $\sigma(F_o)$ is the estimated standard deviation in $|F_{obs.}|$ based on counting statistics. This gave a satisfactory weight analysis. The refinement converged at R 0.067 (R' 0.070), and a final electron-density difference

TABLE 1

Atomic positional parameters (fractional co-ordinates) with standard deviations in parentheses

Atom	x	y	z
(*a*) Molecule 1			
Ru(CO)$_2$ groups			
Ru(1)	0.641 4(2)	0.986 0(1)	0.591 0(2)
C(11)	0.481(4)	0.982(2)	0.682(3)
O(11)	0.395(3)	0.975(1)	0.745(2)
C(12)	0.651(4)	1.067(2)	0.617(3)
O(12)	0.661(3)	1.118(1)	0.630(2)
Ru(2)	0.426 0(3)	1.000 0	0.360 5(2)
C(21)	0.273(3)	0.995(2)	0.446(2)
O(21)	0.172(3)	0.986(1)	0.496(2)
C(22)	0.436(4)	1.079(2)	0.380(3)
O(22)	0.444(3)	1.132(1)	0.398(2)
GeMe$_3$ groups			
Ge(1)	0.787 6(4)	0.979 5(2)	0.795 4(4)
C(101)	0.990(5)	1.003(2)	0.783(4)
H(1011)	0.997	1.038	0.746
H(1012)	0.973	0.971	0.724
H(1013)	1.048	0.997	0.856
C(102)	0.777(5)	0.995(2)	0.864(4)
H(1021)	0.802	0.869	0.820
H(1022)	0.672	0.892	0.882
H(1023)	0.826	0.897	0.950
C(103)	0.727(5)	1.027(2)	0.914(4)
H(1031)	0.631	1.016	0.928
H(1032)	0.726	1.068	0.891
H(1033)	0.782	1.026	0.996
Ge(2)	0.237 4(4)	1.025 3(2)	0.109 3(4)
C(201)	0.118(6)	0.968(2)	0.162(5)
H(2011)	0.064	0.955	0.235
H(2012)	0.156	0.928	0.141
H(2013)	0.035	0.972	0.097
C(202)	0.321(4)	1.051(2)	0.048(3)
H(2021)	0.381	1.014	0.018
H(2022)	0.390	1.080	0.058
H(2023)	0.255	1.057	−0.024
C(203)	0.118(5)	1.092(2)	0.227(4)
H(2031)	0.173	1.124	0.249
H(2032)	0.070	1.079	0.299
H(2033)	0.043	1.100	0.165
Pentalene			
C(121)	0.796(3)	0.975(1)	0.454(3)
C(122)	0.806(3)	0.928(1)	0.544(3)
C(123)	0.678(4)	0.895(2)	0.526(3)
C(124)	0.595(3)	0.918(1)	0.409(3)
C(125)	0.478(4)	0.908(2)	0.314(3)
C(126)	0.502(4)	0.943(2)	0.220(3)
C(127)	0.605(3)	0.982(2)	0.251(3)
C(128)	0.678(3)	0.965(1)	0.366(3)
H(121)	0.863	1.007	0.457
H(122)	0.889	0.919	0.608
H(123)	0.642	0.866	0.580
H(125)	0.397	0.880	0.327
H(126)	0.446	0.935	0.138
H(127)	0.626	1.015	0.203
(*b*) Molecule 2			
Ru(CO)$_2$ groups			
Ru(3)	0.214 0(3)	0.752 6(1)	0.669 3(2)
C(31)	0.072(4)	0.757(2)	0.757(4)
O(31)	−0.027(3)	0.762(1)	0.819(2)
C(32)	0.229(4)	0.673(2)	0.686(4)
O(32)	0.243(3)	0.621(1)	0.699(2)
Ru(4)	0.010 2(3)	0.740 0(1)	0.431 9(2)
C(41)	−0.139(4)	0.750(2)	0.517(3)
O(41)	−0.239(2)	0.749(1)	0.573(2)
C(42)	0.012(4)	0.663(2)	0.448(3)
O(42)	0.017(2)	0.610(1)	0.457(2)
GeMe$_3$ groups *			
Ge(3)	0.359 1(4)	0.752 1(2)	0.873 1(3)
C(301)	0.559(5)	0.739(2)	0.863(4)
H(3011)	0.600	0.761	0.820
H(3012)	0.565	0.695	0.837
H(3013)	0.615	0.733	0.949
C(302)	0.296(5)	0.694(2)	0.977(4)
H(3021)	0.300	0.654	0.948
H(3022)	0.194	0.699	0.993
H(3023)	0.347	0.692	1.062
C(303)	0.341(6)	0.829(2)	0.956(5)
Ge(4)	−0.177 6(4)	0.716 5(2)	0.259 4(4)
C(401)	−0.097(5)	0.690(2)	0.120(4)
H(4011)	−0.147	0.704	0.053
H(4012)	−0.127	0.644	0.121
H(4013)	−0.002	0.682	0.101
C(402)	−0.312(6)	0.664(2)	0.300(5)
H(4021)	−0.392	0.647	0.239
H(4022)	−0.334	0.650	0.377
H(4023)	−0.217	0.655	0.275
C(403)	−0.219(5)	0.790(2)	0.213(4)
H(4031)	−0.316	0.813	0.278
H(4032)	−0.373	0.785	0.154
H(4033)	−0.198	0.784	0.196
Pentalene			
C(341)	0.238(4)	0.845(2)	0.604(3)
C(342)	0.364(4)	0.818(2)	0.632(3)
C(343)	0.386(3)	0.773(1)	0.548(3)
C(344)	0.266(3)	0.776(1)	0.456(3)
C(345)	0.207(3)	0.759(2)	0.336(3)
C(346)	0.089(4)	0.797(2)	0.298(3)
C(347)	0.063(3)	0.837(1)	0.400(2)
C(348)	0.174(3)	0.827(1)	0.497(3)
H(341)	0.208	0.875	0.658
H(342)	0.431	0.825	0.704
H(343)	0.462	0.741	0.557
H(345)	0.241	0.725	0.283
H(346)	0.031	0.790	0.216
H(347)	−0.016	0.864	0.391

* Atoms H(3031)—H(3033) were not located.

---

[7] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[8] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[9] R. F. Stewart, E. R. Davidson, and W. Simpson, *J. Chem. Phys.*, 1968, **42**, 3175.

TABLE 2

Interatomic distances (Å) and bond angles (°)

(*a*) Distances

Molecule 1		Molecule 2	
Ru(1)–Ru(2)	3.060(4)	Ru(3)–Ru(4)	3.056(4)
Ru(1)–Ge(1)	2.491(5)	Ru(3)–Ge(3)	2.476(4)
Ru(2)–Ge(2)	2.482(5)	Ru(4)–Ge(4)	2.486(5)
$Ru(CO)_2$ groups			
Ru(1)–C(11)	1.90(4)	Ru(3)–C(31)	1.74(4)
Ru(1)–C(12)	1.85(4)	Ru(3)–C(32)	1.80(3)
Ru(2)–C(21)	1.81(4)	Ru(4)–C(41)	1.80(3)
Ru(2)–C(22)	1.79(4)	Ru(4)–C(42)	1.74(3)
C(11)–O(11)	1.14(4)	C(31)–O(31)	1.22(5)
C(12)–O(12)	1.17(5)	C(32)–O(32)	1.18(5)
C(21)–O(21)	1.17(4)	C(41)–O(41)	1.18(4)
C(22)–O(22)	1.23(5)	C(42)–O(42)	1.20(4)
$GeMe_3$ groups			
Ge(1)–C(101)	2.00(5)	Ge(3)–C(301)	1.92(5)
Ge(1)–C(102)	1.84(5)	Ge(3)–C(302)	1.88(5)
Ge(1)–C(103)	1.83(5)	Ge(3)–C(303)	1.97(6)
Ge(2)–C(201)	1.72(5)	Ge(4)–C(401)	1.89(5)
Ge(2)–C(202)	1.92(4)	Ge(4)–C(402)	1.82(5)
Ge(2)–C(203)	1.95(4)	Ge(4)–C(403)	2.01(5)
Pentalene			
Ru(1)–C(121)	2.23(3)	Ru(3)–C(341)	2.25(4)
Ru(1)–C(122)	2.13(3)	Ru(3)–C(342)	2.12(4)
Ru(1)–C(123)	2.22(3)	Ru(3)–C(343)	2.26(3)
Ru(1)–C(124)	2.52(3)	Ru(3)–C(344)	2.51(3)
Ru(1)–C(128)	2.58(3)	Ru(3)–C(348)	2.52(3)
Ru(2)–C(125)	2.20(4)	Ru(4)–C(345)	2.28(3)
Ru(2)–C(126)	2.20(4)	Ru(4)–C(346)	2.15(4)
Ru(2)–C(127)	2.23(3)	Ru(4)–C(347)	2.29(3)
Ru(2)–C(124)	2.46(3)	Ru(4)–C(344)	2.52(3)
Ru(2)–C(128)	2.49(3)	Ru(4)–C(348)	2.55(3)
C(121)–C(122)	1.43(5)	C(341)–C(342)	1.34(5)
C(122)–C(123)	1.41(5)	C(342)–C(343)	1.41(5)
C(123)–C(124)	1.51(4)	C(343)–C(344)	1.42(4)
C(124)–C(128)	1.43(5)	C(344)–C(348)	1.53(4)
C(128)–C(121)	1.40(4)	C(348)–C(341)	1.31(5)
C(124)–C(125)	1.44(5)	C(344)–C(345)	1.42(4)
C(125)–C(126)	1.34(5)	C(345)–C(346)	1.42(5)
C(126)–C(127)	1.32(5)	C(346)–C(347)	1.49(5)
C(127)–C(128)	1.42(4)	C(347)–C(348)	1.43(4)

(*b*) Angles

$Ru(CO)_2$ groups			
Ge(1)–Ru(1)–Ru(2)	171.7(2)	Ge(3)–Ru(3)–Ru(4)	172.2(2)
Ge(2)–Ru(2)–Ru(1)	170.9(1)	Ge(4)–Ru(4)–Ru(3)	169.8(2)
Ge(1)–Ru(1)–C(11)	84.7(9)	Ge(3)–Ru(3)–C(31)	82.8(12)
Ru(2)–Ru(1)–C(11)	87.3(10)	Ru(4)–Ru(3)–C(31)	92.0(13)
Ge(1)–Ru(1)–C(12)	84.7(10)	Ge(3)–Ru(3)–C(32)	82.8(12)
Ru(2)–Ru(1)–C(12)	92.3(10)	Ru(4)–Ru(3)–C(32)	91.6(13)
C(11)–Ru(1)–C(12)	89.4(15)	C(31)–Ru(3)–C(32)	92.9(19)
Ru(1)–C(11)–O(11)	172(3)	Ru(3)–C(31)–O(31)	178(4)
Ru(1)–C(12)–O(12)	177(3)	Ru(3)–C(32)–O(32)	178(3)
Ge(2)–Ru(2)–C(21)	82.3(9)	Ge(4)–Ru(4)–C(41)	84.1(10)
Ru(1)–Ru(2)–C(21)	92.9(7)	Ru(3)–Ru(4)–C(41)	89.5(10)
Ge(2)–Ru(2)–C(22)	83.2(10)	Ge(4)–Ru(4)–C(42)	82.3(10)
Ru(1)–Ru(2)–C(22)	89.1(10)	Ru(3)–Ru(4)–C(42)	90.5(10)
C(21)–Ru(2)–C(22)	91.8(16)	C(41)–Ru(4)–C(42)	94.0(16)
Ru(2)–C(21)–O(21)	173(3)	Ru(4)–C(41)–O(41)	172(3)
Ru(2)–C(22)–O(22)	177(3)	Ru(4)–C(42)–O(42)	178(3)
$GeMe_3$ groups			
Ru(1)–Ge(1)–C(101)	110(1)	Ru(3)–Ge(3)–C(301)	113(1)
Ru(1)–Ge(1)–C(102)	112(1)	Ru(3)–Ge(3)–C(302)	112(1)
Ru(1)–Ge(1)–C(103)	115(1)	Ru(3)–Ge(3)–C(303)	110(1)
Ru(2)–Ge(2)–C(201)	111(2)	Ru(4)–Ge(4)–C(401)	112(1)
Ru(2)–Ge(2)–C(202)	111(1)	Ru(4)–Ge(4)–C(402)	114(2)
Ru(2)–Ge(2)–C(203)	113(1)	Ru(4)–Ge(4)–C(403)	109(1)
C(101)–Ge(1)–C(102)	112(2)	C(301)–Ge(3)–C(302)	108(2)
C(102)–Ge(1)–C(103)	102(2)	C(302)–Ge(3)–C(303)	106(2)
C(103)–Ge(1)–C(101)	106(2)	C(303)–Ge(3)–C(301)	107(2)
C(201)–Ge(2)–C(202)	114(2)	C(401)–Ge(4)–C(402)	110(2)
C(202)–Ge(2)–C(203)	104(2)	C(402)–Ge(4)–C(403)	104(2)
C(203)–Ge(2)–C(201)	104(2)	C(403)–Ge(4)–C(401)	108(2)

TABLE 2 (*Continued*)

Pentalene			
C(121)–C(122)–C(123)	108(3)	C(341)–C(342)–C(343)	113(3)
C(122)–C(123)–C(124)	107(3)	C(342)–C(343)–C(344)	105(3)
C(123)–C(124)–C(128)	106(3)	C(343)–C(344)–C(348)	104(2)
C(124)–C(128)–C(121)	108(3)	C(344)–C(348)–C(341)	108(3)
C(128)–C(121)–C(122)	110(3)	C(348)–C(341)–C(342)	110(3)
C(125)–C(124)–C(123)	147(3)	C(345)–C(344)–C(343)	146(3)
C(127)–C(128)–C(121)	146(3)	C(347)–C(348)–C(341)	146(3)
C(125)–C(126)–C(127)	112(3)	C(345)–C(346)–C(347)	110(3)
C(126)–C(127)–C(128)	108(3)	C(346)–C(347)–C(348)	107(2)
C(127)–C(128)–C(124)	106(3)	C(347)–C(348)–C(344)	106(2)
C(128)–C(124)–C(125)	106(3)	C(348)–C(344)–C(345)	108(3)
C(124)–C(125)–C(216)	107(3)	C(344)–C(345)–C(346)	108(3)

TABLE 3

Equations of some least-squares planes and lines: the distances (Å) of relevant atoms from these planes are given in square brackets

Plane (1): C(121), C(122), C(123), C(124), C(128)
$-5.242x + 14.162y + 6.624z = 12.596$
[Ru(1) 1.94]

Plane (2): C(124), C(125), C(126), C(127), C(128)
$-5.966x + 14.882y + 5.222z = 12.256$
[Ru(2) 1.97]

Plane (3): C(341), C(342), C(343), C(344), C(348)
$5.149x + 15.043y - 6.231z = 10.212$
[Ru(3) −1.96]

Plane (4): C(344), C(345), C(346), C(347), C(348)
$6.037x + 15.091y - 4.922z = 11.069$
[Ru(4) −1.97]

Plane (5): Ru(1), C(11), C(12)
$4.893x - 3.302y + 8.479z = 4.894$

Plane (6): Ru(2), C(21), C(22)
$4.865x - 2.725y + 8.547z = 2.428$

Plane (7): Ru(3), C(31), C(32)
$5.187x + 2.711y + 8.264z = 8.681$

Plane (8): Ru(4), C(41), C(42)
$4.976x + 1.894y + 8.501z = 5.124$

Line (9): Ru(1), Ru(2)
$x = 0.534 + 0.070t;\ y = 0.993 - 0.004t;\ z = 0.476 + 0.075t$

Line (10): Ru(3), Ru(4)
$x = 0.112 + 0.067t;\ y = 0.746 + 0.004t;\ z = 0.551 + 0.078t$

Angles (°) between least-squares planes and lines:

(1)—(2)	170.6	(5)—(6)	1.5	(9)—(1)	86.1
(3)—(4)	170.7	(7)—(8)	2.7	(9)—(2)	84.6
(9)—(5)	3.6	(10)—(3)	85.5	(10)—(7)	2.6
(9)—(6)	3.1	(10)—(4)	85.3	(10)—(8)	0.6

synthesis showed no peaks >0.9 or <-0.4 e Å^{-3}. The structure was refined in both enantiomorphs; the coordinates given in Table 1 gave the better refinement and correspond, we believe, to the actual structure of the crystal examined. Positional parameters are in Table 1, interatomic distances in Table 2, and some least-squares planes, with interplanar angles, in Table 3. All the computational work was carried out at the University of London Computing Centre with the '*X*-Ray' system of programs.[10] Observed and calculated structure factors, and all thermal parameters, are listed in Supplementary Publication No. SUP 22203 (16 pp.).*

---

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

[10] Technical Report TR 192, Computer Science Center, University of Maryland, June 1972.

DISCUSSION

The crystal-structure determination shows that the $[Ru_2(GeMe_3)_2(CO)_4(C_8H_6)]$ molecule contains a pentalene species with each five-membered ring bonded to a ruthenium atom. The overall molecular configuration, with the atom-numbering system, is given in Figure 1. The spine of the molecule comprises the metal-atom sequence Ge–Ru–Ru–Ge and is significantly non-linear (Ge–Ru–Ru 171°); the Ru–Ge bonds are directed slightly (but symmetrically) away from the molecular centre. The pentalene is likewise significantly non-planar, with the two planar five-membered rings hinged to one another at an angle of 173° (Table 3), again away from the molecular centre. Figure 2 shows the relation between the pentalene species and the metal-atom chain. There is no imposed crystallographic symmetry, but each of the two independent molecules in the asymmetric unit possesses approximate mirror symmetry about the plane perpendicular to, and through the midpoint of, the Ru–Ru bond; *i.e.* the $GeMe_3$ groups take up an eclipsed configuration.

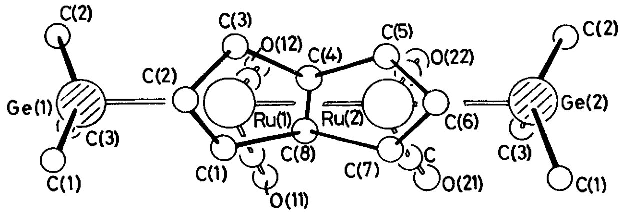

FIGURE 1 Molecular configuration of $[Ru_2(GeMe_3)_2(CO)_4(C_8H_6)]$ showing the atom-numbering sequence of the pentalene ligand. In molecule 1 the ruthenium atoms are labelled Ru(1) and Ru(2); atoms bonded to Ru(1) and Ge(1) are prefixed 1 and 10 respectively, while atoms of the pentalene ligand are prefixed 12. In molecule 2 prefixes 3 and 4 are used similarly

The Ru–Ru bond [mean 3.058(4) Å] is long in comparison with those contained in most other binuclear unbridged, carbonyl-bridged, or organo-ligand-bridged species. For example, distances have been reported of 2.943(1) Å in $[Ru_2(SnMe_3)_2(CO)_8]$,[11] 2.735(2) Å in $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$,[12] 2.865(2) Å in $[Ru_2(CO)_6(C_6H_6)]$,[13] 2.845(1) Å in $[Ru_2(CO)_5(C_{18}H_{13})]$,[14] and 2.937(1) Å in $[Ru_2(SiMe_3)_2(CO)_5\{C_7H_6(SiMe_3)\}]$.[15] Measurements of Ru–Ge distances are scarce, but the value obtained for the title complex [mean 2.484(5) Å] agrees closely with that found in $[\{Ru(GeMe_2)(CO)_3\}_3]$ (though here the Ge atoms bridge the Ru–Ru bonds),[16] and is, as expected, *ca.* 0.1 Å longer than known Fe–Ge distances.[17,18] On the basis of covalent radii, however, the bond seems rather short (Ru 1.42, Ge 1.22 Å) and compensates for the long Ru–Ru bond. The Ge–Me and Ru–C–O distances are all normal.

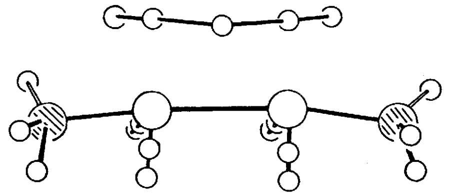

FIGURE 2 Section through the $[Ru_2(GeMe_3)_2(CO)_4(C_8H_6)]$ molecule to show the non-linear spine and the non-coplanar rings of the pentalene

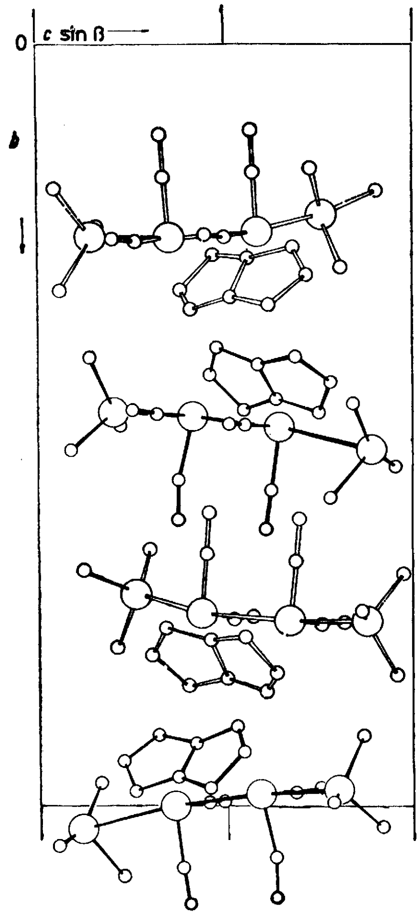

FIGURE 3 Contents of one unit cell viewed in projection down *a* looking towards the origin

Pentalene-carbon–ruthenium distances fall into two sets, the two carbon atoms at the ring junction being further from the two Ru atoms than are the non-bridging carbon atoms, despite the slight favourable fold in the pentalene molecule. Atoms C(1)–C(3) and C(5)–C(7) (ignoring the numbering prefixes 12 for molecule 1 and 34 for molecule 2) can be simplistically regarded as being components of interannular η-allyl units bonded to their respective Ru atoms, while C(4) and C(8) and the two

---

[11] J. A. K. Howard, S. C. Kellett, and P. Woodward, *J.C.S. Dalton*, 1975, 2332.

[12] O. S. Mills and J. P. Nice, *J. Organometallic Chem.*, 1967, **9**, 339.

[13] F. A. Cotton and W. T. Edwards, *J. Amer. Chem. Soc.*, 1968, **90**, 5412.

[14] U. Behrens and E. Weiss, *J. Organometallic Chem.*, 1974, **73**, C67.

[15] J. A. K. Howard and P. Woodward, *J.C.S. Dalton*, 1975, 59.

[16] J. A. K. Howard and P. Woodward, *J. Chem. Soc.* (*A*), 1971, 3648.

[17] E. H. Brooks, M. Elder, W. A. G. Graham, and D. Hall, *J. Amer. Chem. Soc.*, 1968, **90**, 3587; M. Elder and D. Hall, *Inorg. Chem.*, 1969, **8**, 1424.

[18] M. A. Bush and P. Woodward, *J. Chem. Soc.* (*A*), 1967, 1833.

Ru atoms are involved in a four-electron multicentre interaction, as proposed for the cyclo-octatetraene complex $[Fe_2(CO)_5(C_8H_8)]$.[19] The mean Ru–C distances are 2.21(1) Å for the η-allyl groups and 2.53(2) Å for the bridge atoms.

Among the Ru–$GeMe_3$ groups there is a tendency, commonly observed, for the C–Ge–C angle to be smaller than the ideal tetrahedral value [mean 107(1)°] and the Ru–Ge–C angle [mean 112(1)°] to be correspondingly greater.

The mode of packing of the molecules in the crystallographic unit cell is drawn in Figure 3. There are no abnormally short intermolecular contacts.

We thank the S.R.C. for support.

[7/1393 *Received*, 1*st August*, 1977]

---

[19] E. B. Fleischer, A. L. Stone, R. B. K. Dewar, J. D. Wright, C. E. Keller, and R. Pettit, *J. Amer. Chem. Soc.*, 1966, **88**, 3158.